1115. *Tracer Studies on Alcohols. Part VI.* The Pinacolic Rearrangement of* cis- *and* trans-1,2-*Dimethylcyclopentane*-1,2-*diol.*

By C. A. Bunton and M. D. Carr.

In aqueous perchloric acid *cis*- and *trans*-1,2-dimethylcyclopentane-1,2-diol are converted, at similar rates, into 2,2-dimethylcyclopentanone and a tar, the latter being the major product from the *trans*-diol. The kinetic form of the decomposition is typical of an *A*-1 reaction. Oxygen exchange between the *trans*-diol and water is *ca.* five times faster than the decomposition, and there is no rearrangement to *cis*-diol. The *cis*-diol does not exchange its oxygen atoms with water, but rearranges to *trans*-diol, ketone, and tar. These observations suggest that two distinct intermediates are involved in these reactions, and that they are not readily interconverted. The tar is soluble in organic solvents, and is an acid–base indicator.

This study of the acid-catalysed rearrangement of *cis*- and *trans*-1,2-dimethylcyclopentane-1,2-diol complements studies on the corresponding cyclohexanediols (Part V). The rates of oxygen exchange and pinacolic rearrangement of these cyclohexane diols can be explained in terms of a common carbonium-ion intermediate, but for the cyclopentane diols we must invoke two distinct intermediates, because the *cis*- and the *trans*-isomer behave very differently. Bartlett and his co-workers[1] found that rearrangement of *cis*-1,2-dimethylcyclopentane-1,2-diol (I) in boiling 30% sulphuric acid gave a good yield of 2,2-dimethylcyclopentanone (II), but that the *trans*-diol (III) was resinified on similar

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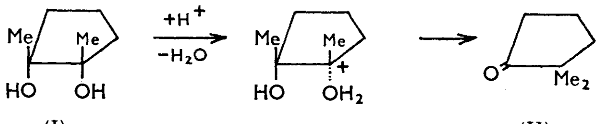
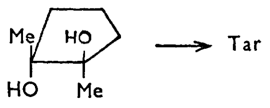
* Part V, preceding paper.

[1] Bartlett and Pöckel, *J. Amer. Chem. Soc.*, 1937, **59**, 820; Bartlett and Bavley, *ibid.*, 1938, **60**, 2416.

treatment.[1] Meerwein [2] isolated a small amount of ketone after reaction of the *trans*-diol under Bartlett's conditions, and a 20% yield of it on rearrangement of the *trans*-diol at −10° in concentrated sulphuric acid. This difference in behaviour was reasonable because in the *cis*-diol (I) a methyl group can migrate readily to the forming carbonium-ion centre.



(I) (II)



(III)

We have confirmed these general observations and find also that the tar contains an acid–base indicator, and that rearrangement of the *trans*- but not of the *cis*-diol is accompanied by extensive oxygen exchange between diol and solvent water.

Kinetics.—The *cis*-diol reacts quantitatively with both periodic acid and lead tetra-acetate, but the *trans*-diol reacts with lead tetra-acetate only.[3,4] Therefore for the *cis*-diol we measure (by periodic acid) the rate of its rearrangement to *trans*-diol as well as to ketone and tar. For the *trans*-diol we measure (by lead tetra-acetate) the rate of rearrangement of (*trans*- + *cis*-)diol, but this sum is of no account, because no *cis*-diol could be detected during reaction of the *trans*-isomer. The values of the first-order rate constant, k, for decomposition of the diols are in Table 1. Plots of log k against Hammett's acidity function,[5a] $-H_0$, are linear with slopes of 1·05 and 1·02 for the *cis*- and the *trans*-diol, respectively; values of w, Bunnett's parameter,[6] are ≈ 0. The entropies and energies of activation are: [5b] for the *cis*-diol, $\Delta S^* = 9{\cdot}3$ e.u., $E = 30$ kcal. mole^{-1}; and for the *trans*-diol $\Delta S^* = 9{\cdot}6$ e.u., $E = 31$ kcal. mole^{-1}. The solvent isotope effect,[5b] $k_{D_2O}/k_{H_2O} = 2{\cdot}1$, for both isomers in 96% D_2O.

TABLE 1.

Rates of decomposition of the diols, at 59·7° unless otherwise specified.

trans-Diol

$[HClO_4]$ (M)	0·987			1·43	2·23	3·09		4·00
10^5k (sec.$^{-1}$)	1·40	8·48 *	18·0 *‡	2·27	7·79	19·3	20·7	56·0
$\log k + H_0 + 6$	0·94	—	—	0·97	1·01	1·10		1·05

cis-Diol

$[HClO_4]$ (M)	0·68		0·95		1·43	1·75		2·67	3·63
10^5k (sec.$^{-1}$)	15·3 †	32·8 †‡	3·61	25·3 †	6·91	9·8	10·6	33·3	90·6
$\log k + H_0 + 6$	—	—	1·36	—	1·35	1·33	1·37	1·45	1·51

* 73·0°; † 74·7°; ‡ D_2O (96%).

Products.—trans-*Diol*. At 59·7° in 3M-perchloric acid, 2,2-dimethylcyclopentanone was formed in *ca.* 5% yield, but <1% was formed in a reaction in 1M-acid (see Experimental section). No *cis*-diol could be detected during the reaction, and the main product was the tar, which had been observed by Bartlett and Bavley [1] (cf. Appendix).

cis-*Diol*. The ketonic rearrangement product was isolated, by gas–liquid chromatography, after reaction in 3M-perchloric acid, at 59·7°, and *ca.* 4% of the *trans*-diol was formed after 50% reaction (Table 2). Some tar was formed, but apparently much less than in the rearrangement of the *trans*-diol.

[2] Meerwein, *Annalen*, 1939, **542**, 123.

[3] Bunton and Carr, *J.*, 1963, 770.

[4] Bulgrin and Dahlgren, *J. Amer. Chem. Soc.*, 1958, **80**, 3883.

[5] (*a*) Long and Paul, *Chem. Rev.*, 1957, **57**, 935; (*b*) Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2363; Pritchard and Long, *ibid.*, 1956, **78**, 6008; 1958, **80**, 4162; Bunton and Shiner, *ibid.*, 1961, **83**, 3207.

[6] Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

TABLE 2.

Interconversion of diols at 59·7°.

cis-Diol; [$HClO_4$] = 1·56M.

Reaction (%)	17	31	52	84
[*trans*] (mole %)	1·6	4·4	4·0	2·4

[$HClO_4$] = 1M. Calc. values for $d[T]/dt \approx 0$.

[*cis*-Diol] (mole %)	66·5	50·7	38·6	25·7
[*trans*-Diol] (mole %)	3·5	4·1	4·3	3·6

Epoxide.—Acid-hydrolysis of 1,2-dimethyl-1,2-epoxycyclopentane gives the *trans*-diol; the rearranged ketone was a possible, but very minor, product (see Experimental section). There was no resinification, but coloured materials could be extracted into chloroform.

Oxygen Exchange.—Oxygen exchange between the *trans*-diol and water is much faster than its decomposition, but the *cis*-diol does not exchange its oxygen atoms (Table 3 and Experimental section).

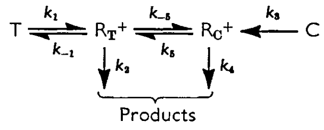
TABLE 3.

Oxygen exchange of the *trans*-diol at 59·7°.

[$HClO_4$] (M)	1·01	2·78
$10^5 k_e$ (sec.$^{-1}$)	7·2	56

Mechanisms of Reaction and Oxygen Exchange.—Although the *cis*-diol gives the rearranged ketone in good yield, whereas the *trans*-diol decomposes largely to tar, the rates of reaction are similar, suggesting that loss of a hydroxyl group is the rate-limiting step in both reactions and is followed by rapid reaction of an intermediate. The variation of rate with acid concentration, the Arrhenius parameters, and the deuterium solvent isotope effects suggest that the decompositions of these diols fall into the *A*-1 mechanistic class.[5,6] The rates of reaction are similar to those of the rearrangement of pinacol [7] and of the 1,2-dimethylcyclohexane-1,2-diols (Part V), although the entropies and energies of activation are slightly smaller for the cyclopentanediols.

The results for the rearrangement and oxygen exchange of the cyclohexanediols could be interpreted in terms of a common carbonium-ion intermediate. Such a simple explanation is inadequate here, because not only do the two diols give different products but they differ strikingly in their rates of oxygen exchange. The simplest scheme for these reactions and isotopic exchanges involves two distinct carbonium ions, which are not rapidly interconverted.



(R_T^+ and R_C^+ are the carbonium ions formed from the *trans*- and the *cis*-diol, T and C, respectively; the rate constants k_1 and k_3 include equilibrium constants for protonation of the diols and depend on acidity.)

We assume that formation of the carbonium ion from the *cis*-diol is irreversible, because there is no oxygen exchange of this diol. The *trans*-diol exchanges its oxygen atoms faster than it decomposes, and $k_{-1} \approx 5k_2$ (Tables 1 and 3). Our evidence is too sparse to permit a general kinetic solution, but by using the rates of oxygen exchange and of chemical reaction we estimate the ratios of some of the rate constants, provided that we assume that R_C^+ and R_T^+ decompose more readily than they are interconverted, *i.e.*, $k_2 \gg k_{-5}$, and $k_4 \gg k_5$.

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[7] Bunton, Hadwick, Llewellyn, and Pocker, *J.*, 1958, 403.

For rearrangement of the *cis*-diol, when the *trans*-diol is at its maximum concentration, d[T]/dt = 0, and the stationary state approximation gives:

$$\mathrm{d}[\mathrm{R_T}^+]/\mathrm{d}t = k_1[\mathrm{T}] - (k_{-1} + k_2)[\mathrm{R_T}^+] + k_5[\mathrm{R_C}^+] = 0. \qquad (1a)$$

$$\mathrm{d}[\mathrm{R_C}^+]/\mathrm{d}t = k_3[\mathrm{C}] - k_4[\mathrm{R_C}^+] + k_{-5}[\mathrm{R_T}^+] = 0. \qquad (1b)$$

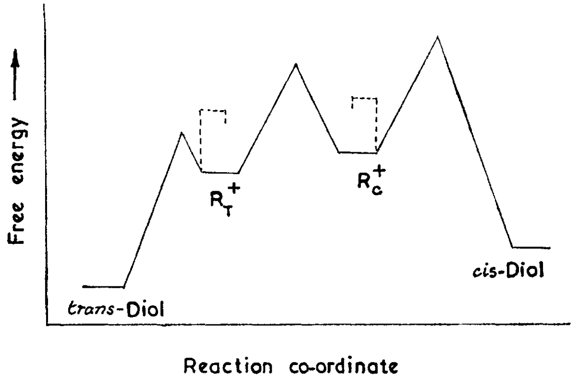
$$\mathrm{d}[\mathrm{T}]/\mathrm{d}t = k_{-1}[\mathrm{R_T}^+] - k_1[\mathrm{T}] = 0. \qquad (1c)$$

Therefore

$$[\mathrm{C}]/[\mathrm{T}] = (k_2/k_{-1})(k_1/k_3)(k_4/k_5). \qquad (2)$$

The sum of the first-order rate constants for oxygen exchange and decomposition of the *trans*-diol (Tables 1 and 3) gives $10^5 k_1 = 8{\cdot}7$ sec.$^{-1}$, at 59·7° in 1M-perchloric acid. Under the same conditions $k_1/k_3 = 8{\cdot}7/3{\cdot}8 = 2{\cdot}3$, and $k_2/k_{-1} = 0{\cdot}2$.

For rearrangement of the *cis*-diol, when d[T]/dt = 0, [C]/[T] $\approx$ 10 [from experiments with 1·5M-acid (Table 2), and with the assumption that the maximum concentration of *trans*-diol will be insensitive to small changes in acidity (cf. Part V)]. Therefore, using equation (2), we estimate $k_4/k_5 \approx 20$. The main sources of error, apart from the assumptions made, is the ratio [C]/[T], which is changing rapidly when d[T]/d$t \approx 0$. However, irrespective of the precision of k_4/k_5, this analysis suggests that the ion $\mathrm{R_C}^+$ forms the products much more readily than it reverts to *cis*-diol or rearranges to the other carbonium ion $\mathrm{R_T}^+$, and that $\mathrm{R_T}^+$ reverts to *trans*-diol more readily than it decomposes to products.



Schematic energy diagram for interconversion of the diols (full line) and for formation of the products (broken line).

We cannot apply this treatment to the decomposition of the *trans*-diol, because no *cis*-diol is formed during this reaction. A crude estimate of the ratio k_2/k_{-5} can be made if we assume that all the ketone which is formed from decomposition of the *trans*-diol comes from $\mathrm{R_T}^+$, whereas $\mathrm{R_C}^+$ gives only the tar. Then d[Ketone]/dt = $k_1k_{-5}[\mathrm{T}]/(k_{-1} + k_2)$; and {from equations (1a and b) when [C] = 0}

$$\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_1k_2[\mathrm{T}]/(k_{-1} + k_2);$$

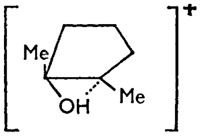
therefore k_{-5}/k_2 is the molar percentage of ketone in the total products.

The yield of ketone from the *trans*-diol decreases with decreasing acidity (and probably with increasing temperature) (cf. refs. 1 and 2), and, although at 59·7° the yield is *ca.* 5%, in 3M-perchloric acid, it is <1% in 1M-acid. Therefore, in 1M-perchloric acid minimum values of $k_2/k_{-5} \approx 100$, and $k_{-1}/k_{-5} \approx 500$.

The value for this ratio is very approximate, but it suggests that the energy barrier for interconversion of the carbonium is greater than those for their decomposition. To the extent that ketone may be formed directly from $\mathrm{R_T}^+$ we underestimate the value of k_2/k_{-5}.

These rate ratios almost certainly depend upon acidity and temperature, and because rearrangement of the *trans*-diol in cold concentrated sulphuric acid gives comparatively large amounts of ketone[2] it seems that interconversion of the carbonium ions occurs most readily in these conditions, relative to their other reactions.

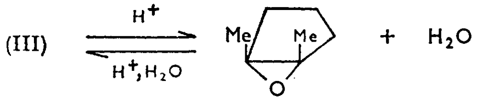
Our conclusions as to the fates of the carbonium ions are summarised qualitatively in a plot of free energy against reaction co-ordinate (see Figure). The broken line represents the energy barriers for the conversion of R_C^+ and R_T^+ into the reaction products, and is in a different dimension to the full line which relates to the interconversion of the diols.



(IV)

It is assumed that decomposition and oxygen exchange of the *trans*-diol involve a common intermediate (cf. above).

The ready reversion of the carbonium ion, R_T^+, into the *trans*-diol suggests that its structure is (IV). Interaction between the hydroxyl group and the carbonium ion centres should inhibit both methyl migration and formation of the *cis*-diols. Oxygen exchange between the *trans*-diol and water could also be caused by formation and hydrolysis of an epoxide:



and we could assume that the *trans*-diol forms both the carbonium ion, R_T^+, and the epoxide, and that the carbonium ion gives only the reaction products, whereas the epoxide reverts to the *trans*-diol. However, this route of exchange is not available for *cis*-1,2-dimethylcyclohexane-1,2-diol (Part V).

The absence of oxygen exchange during rearrangement of the *cis*-diol was unexpected, and this result suggests that migration of the methyl group to the carbonium ion centre occurs very soon after breaking of the carbon–oxygen bond, but interaction between the methyl group and the carbonium-ion centre is not strong enough to suppress completely the rearrangement of the carbonium ion, R_C^+, to the other ion R_T^+.

From the rates of rearrangement and oxygen exchange for pinacol and the cyclic diols (Tables 1 and 3, and Part V) we calculate rate constants, k_1 or k_3, for breaking of the carbon–oxygen bonds. These rate constants (Table 4) differ from the rate constants, k, for rearrangement or decomposition, because they take into account return of the carbonium ions to the diols.

The values of k for the *cis*-diols were determined by using periodic acid, and therefore measure the rates of formation of both rearrangement products and *trans*-diol, but those for the *trans*-diols were determined by using lead tetra-acetate, and therefore measure only the formation of the rearrangement products. For this reason, in calculating k_1 for *trans*-1,2-dimethylcyclohexane-1,2-diol we must take into account partitioning of its carbonium ion between *trans*- and *cis*-diol and ketone (Part V). The rate constants, k_1 and k_3, for these diols are so similar that interactions between a neighbouring alkyl or hydroxyl group and the forming carbonium-ion centre can give little or no assistance to

TABLE 4.

Relative reactivites of 1,2-diols in M-$HClO_4$ at 59·7°.

	1,2-Dimethylcyclohexane		1,2-Dimethylcyclopentane		
1,2-Diol	*trans*-	*cis*-	*trans*-	*cis*-	Pinacol[7]
10^5k (sec.$^{-1}$)............	1·85	0·89	1·45	3·80	0·44
10^5k_1 or $10^5\,k_3$ (sec.$^{-1}$)	4·2	1·2	8·7	3·8	1·5 *

* Calc. on the assumption that the relative rates of exchange and hydrolysis are insensitive to small changes in temperature and acidity.[7]

bond-breaking. A similar conclusion had been reached from comparisons of the reactivities of pinacol and t-butyl alcohol.[7] Migration to the carbonium-ion centre, therefore, occurs after the transition state for bond-breaking has been reached. There is no unique mechanism of the pinacol–pinacone rearrangement. In some reactions, the diols are in equilibrium with their slowly rearranging carbonium ions;[8] in others, group migration occurs soon after bond-breaking; and in yet others these two processes are simultaneous. Rate measurements, by themselves, do not generally differentiate between these possibilities. The quantitative formation of the *trans*-diol by the rapid acid-hydrolysis of the epoxide shows that a carbonium ion is not an intermediate (cf. ref. 9 and Part V).

EXPERIMENTAL

Materials.—The *trans*-diol was prepared by hydroxylation of 1,2-dimethylcyclopentene with peroxyformic acid[10] and after recrystallisation had m. p. 101° (lit.,[4] 101·6°,[11] 105—107°). The *cis*-diol was prepared from the olefin and osmium tetroxide;[4,11] when purified by vacuum-distillation, it had b. p. 107°/20 mm., m. p. 20° (lit.,[4] 20·5—20·8°, [11] 25°). This diol is very hygroscopic, and we could not raise its m. p. by recrystallising it from cold pentane or ethyl acetate. Our sample of the *cis*-diol was oxidised quantitatively by both periodic acid and lead tetra-acetate; the *trans*-diol was inert to periodic acid but was oxidised quantitatively by lead tetra-acetate.

1,2-Epoxy-1,2-dimethylcyclopentane was prepared from the cyclopentene[3] and peroxyoctanoic acid.[12] It was fractionally distilled through a helix-packed column, and the fraction of b. p. 123—125° was purified by gas–liquid chromatography on a Tween–Celite column.

Kinetics.—Decomposition of the diols was followed by estimation of the *trans*-diol with lead tetra-acetate, and of the *cis*-diol with periodic acid. The general procedure was that described in Part V, except that insoluble tars were filtered off before addition of the oxidant. Reaction was followed for up to two half-lives; plots of log [Diol] against time were linear.

Products.—The main product of the *trans*-diol is a black tar.[1] However, 2,2-dimethylcyclopentanone was isolated from both diols by gas–liquid chromatography and gave the semicarbazone, m. p. 192° (lit.,[1,2] 193—194°). We did not attempt to isolate the ketone quantitatively from the reaction of the *cis*-diol, where it is the major product,[1] but its yield from reaction of the *trans*-diol is 5% in 3M-perchloric acid at 59·7°, and <1% in 1M-acid (estimated by gas–liquid chromatography).

The amount of interconversion of the diols was determined by the methods described in Part V, although the coloured products made the analysis less satisfactory for the dimethylcyclopentanediols. However, the evidence for the absence of *cis*-diol during rearrangement of the *trans*-isomer is good, because it is easy to estimate small amounts of the *cis*-diol with periodic acid. [The greater rate of rearrangement of the *cis*- than of the *trans*-diol (Table 1) limits the amount that could be detected.]

Hydrolysis of the epoxide is very rapid in 0·2M-perchloric acid at room temperature, although the epoxide is insoluble in water. After complete reaction the cloudy solution was extracted with pentane, and gas–liquid chromatography of this extract gave a small peak whose retention time was similar to that of 2,2-dimethylcyclopentanone. That ketone, if formed, was obtained in less than 3% yield. Extraction of the aqueous layer with chloroform gave the *trans*-diol, m. p. 100°, with an infrared spectrum identical with that of authentic material. Analysis of the reaction mixture showed that the *trans*-diol was formed in >95% yield, and there was no evidence for the *cis*-diol.

Oxygen Exchange.—The method was that described in Part V, although it was slightly simplified because no *cis*-diol was formed during rearrangement of the *trans*-diol.

The first-order rate constant for oxygen exchange, k_e, was calculated from:

$$tk_e = 2 \ln [N_\infty/(N_\infty - N_t)]$$

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[8] Collins, *Quart. Rev.*, 1960, **14**, 357.

[9] Parker and Isaacs, *Chem. Rev.*, 1959, **59**, 737; Koskikallio and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 815; Kwart and Goodman, *J. Amer. Chem. Soc.*, 1960, **82**, 1947.

[10] Roebuck and Adkins, *Org. Synth.*, 1948, **28**, 35.

[11] Rocek and Westheimer, *J. Amer. Chem. Soc.*, 1962, **84**, 2241.

[12] Parker, Ricciuti, Ogg, and Swern, *J. Amer. Chem. Soc.*, 1955, **77**, 4037.

where N_∞ and N_t are the abundances of the diol in atom % excess, calculated for complete exchange and at time *t*. Two examples are tabulated.

trans-Diol in 1·01M-$HClO_4$ at 59·7°.

Time (hr.)	Reaction (%)	N_{H_2O}	N	Exchange (%)
1·5	9	1·61	0·29	18
4·0	19	2·78	1·01, 1·10, 1·19	39·5
4·0	19	1·61	0·65, 0·66	40·5
8·0	34	1·61	1·00, 1·05	64

(Duplicate values of *N* are for separate samples of diol.)

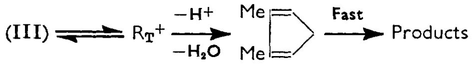
cis-Diol in 0·98M-$HClO_4$ at 59·7°. $N_{H_2O} = 1{\cdot}61$.

Time (hr.)	Reaction (%)	N	Exchange (%) *
1·0	18	0·048	1·5
2·5	32	0·047	−1
6·0	60	0·096	1

* Corrected for *trans*-diol on the assumption that it is 50% enriched.

APPENDIX

The Coloured Products.—The coloured tar which is the main decomposition product of the *trans*-diol is not formed directly from the diol, because the decomposition follows a first-order rate law. It is, therefore, probably formed from some readily polymerisable material which is itself formed from the carbonium ion. Bartlett and Bavley suggested that dimethylcyclopentadiene, formed by dehydration of the diol, rapidly polymerised, *e.g.*:



but they were unable to trap any dimethylcyclopentadiene.[1]

Coloured tars are also formed from 1,2-dimethylcyclopentene and hydrogen bromide.[13] It seemed possible that the tar might also be formed from 2,2-dimethylcyclopentanone, by an acid-catalysed aldol condensation. Therefore, various organic compounds (0·1 g.) were dissolved in 10 c.c. of 3M-perchloric acid and left for 2 hr. at 59·7°. The solutions were then extracted with 25 c.c. of chloroform. The ketone in acid does not give colours, but strong colours are formed from the *trans*-diol or 1,2-dimethylcyclopentene in acid, or from mixtures of them in acid. The chloroform extract from the *trans*-diol has sharp absorption bands at 330 and 470 mμ, and a broad band between 600 and 800 mμ. This broad band is also shown by the chloroform extract of the cyclopentene, but instead of the peak at 475 mμ there is a sharply increasing absorption below *ca.* 450 mμ with a shoulder at *ca.* 280 mμ.

The coloured material is an indicator; the chloroform extract from acid is deep green, from neutral solution bright orange, and from alkali pale yellow. These colour changes are reversible and the *cis*-diol gives similar solutions, less intense than those from the *trans*-diol or olefin. The colour change of the indicator is at pH ~ 2. The chloroform extract from an alkaline solution has no absorption peak, but a gradually increasing absorption towards the lower wavelengths. Acid-hydrolysis of the epoxide gives no tar, but the chloroform extract is coloured. We do not know whether this colour is formed directly from the epoxide or from the *trans*-diol.

Wassermann and his co-workers [14] have shown that cyclopentadiene gives coloured polymers in aprotic solvents containing trichloro- or trifluoro-acetic acid, and it is probable that the indicator which we observe is similar to these polymeric cyclopentadienes.

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[*Received, April* 4*th*, 1963.]

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[13] Collins and Hammond, *J. Amer. Chem. Soc.*, 1960, **82**, 4323.
[14] French, Roubinek, and Wassermann, *J.*, 1961, 1953.